Atty. Docket #: S-98/24

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

INTERNATIONAL APPL. NO.: PCT/EP99/07782	:	
INTERNATIONAL FILING DATE: -10/11/99-	:	
APPLICANT: VINCENT WILMET ET AL	:	
SERIAL NO:	:	**ART UNIT:**
FILED: -HEREWITH-	:	**EXAMINER:**
FOR: "HYDROFLUORINATION CATALYST AND PROCESS"	:	
	:	

Commissioner for Patents
Box PCT
Washington, D.C. 20231

"Express Mail" No.: EE617838364 **Date:** - APRIL 11, 2001 -

I hereby certify that this paper, along with any other paper or fee referred to in this paper as being transmitted herewith, is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, postage prepaid, on the date indicated above, addressed to the Commissioner for Patents, Washington, D.C. 20231

-Carrie A. McPherson-
(Typed or printed name of mailing paper or fee)

Carrie A. McPherson
(Signature of person mailing paper)

TRANSMITTAL OF APPLICATION PAPERS TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371 (37 CFR 1.494 OR 1.495)

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. [X] This is a FIRST submission of items concerning a filing under 35 U.S.C. §371.

2. [ ] This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371.

3. [X] This is an express request to begin national examination procedures (35 U.S.C. §371[f]) at any time rather than delay.

4. [X] A proper Demand for International Preliminary Examination (IPE) was made to the appropriate Authority (IPEA) within the time period required.

5. [X] A copy of the International Application as filed (35 U.S.C. §371[c][2]) --
   a. [X] is transmitted herewith (required when not transmitted by International Bureau).
   b. [ ] has been transmitted by the International Bureau. See WIPO Publication WO 00/21660.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).

6. [X] A (verified) translation of the International Application into the English language is enclosed.

7. [ ] Amendments to the (specification and) claims of the International Application under PCT Article 19 (35 U.S.C. 371[c][3])
   a. [ ] are transmitted herewith (required if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
   e. [ ] will be submitted with the appropriate surcharge.

8. [ ] A translation of the amendments to the claims (and/or the specification) under PCT Article 19 (35 U.S.C. §371[c][3]) is enclosed or will be submitted with the appropriate surcharge.

9. [X] An oath or declaration/power of attorney of the inventor(s) (35 U.S.C. §371[c][4]) will follow.
   [ ] and is attached to the translation of (or a copy of) the International Application.
   [ ] and is attached to the substitute specification.

10. [ ] A translation of at least the Annexes to the IPE Report under PCT Article 36 (35 U.S.C. §371[c][5]) is enclosed.

Items 11. to 16. below concern other document(s) or information included:

11. [X] An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.

12. [X] An Assignment for recording and a separate cover sheet in compliance with 37 CFR 3.28 and 3.31 will follow.

13. [X] A FIRST preliminary amendment is enclosed.
    A SECOND or SUBSEQUENT preliminary amendment is enclosed.

14. [ ] A substitute specification (including claims, abstract, drawing) is enclosed.

15. [ ] A change of power of attorney and/or address letter is enclosed.

16. [X] Other items of information:

    [X] This application is being filed pursuant to 37 CFR 1.494(c) or 1.495(c), and any missing parts will be filed before expiration of--

        [ ] 22 months from the priority date under 37 CFR 1.494(c), or

        [X] 32 months from the priority date under 37 CFR 1.495(c).

    [X] The undersigned attorney is authorized by the International applicant and by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c) or 1.495(c).

The following additional information relates to the International Application:

- [X] Receiving Office: EPO
- [X] IPEA (if filing under 37 CFR 1.495): EPO
- [X] Priority Claim(s) (35 USC §§ 119, 365):
  Belgium Appln. 98 00732 filed -October 12, 1998-.
- [X] A copy of the International Search Report is
  - [ ] enclosed.
  - [X] attached to the copy of the International Application.
- [X] A copy of the Receiving Office Request Form is enclosed. [In French]
- [X] Form PCT/IPEA/409 - (6) pages [In French]
- [X] Form PTO/SB/05 (1) sheet

The fee calculation is set forth on the next page of this Transmittal Letter.

FEE CALCULATION SHEET

[x] A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee.....	$ 860.00
Total Number of claims in excess of (20) times $18.....	-0-
Number of independent claims in excess of (3) times $80.....	-0-
Fee for multiple dependent claims $270.....	-0-
TOTAL FILING FEE...	$ 860.00

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By _____
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AIP/cam (5129*47)
Enclosures
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S-98/24 (5129*47)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: VINCENT WILMET *ET AL.*	
SERIAL NO. TO BE ASSIGNED	ART UNIT: TO BE ASSIGNED
INTERNATIONAL APPL. NO. PCT/EP99/07782	EXAMINER: TO BE ASSIGNED
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FOR: HYDROFLUORINATION CATALYST AND PROCESS	

Asst. Commissioner for Patents
Washington, D.C. 20231

"EXPRESS MAIL" NO. EE617838364 DATE: APRIL 11, 2001
I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231

CARRIE A. MCPHERSON
(TYPED OR PRINTED NAME OF PERSON MAILING PAPER OR FEE)

Carrie A. McPherson
(SIGNATURE OF PERSON MAILING PAPER OR FEE)

PRELIMINARY AMENDMENT

Sir:

Prior to fee calculation and examination please amend the above-identified application as follows.

In the Claims

Please cancel claims 1-10.

Please add the following new claims 11-20.

--11. A hydrofluorination catalyst based on chromium oxide which is depleted in ammonium salt and which exhibits a content of ammonium salts of less than or equal to 0.2% by weight,

expressed in the form of NH_4^+, with respect to the content of chromium in the catalyst, expressed in the form of Cr_2O_3.

12. The catalyst according to claim 11, in which the content of ammonium salts is less than or equal to 0.1% by weight of ammonium salts.

13. The catalyst according to claim 11, additionally comprising other metals or salts of other metals and their mixtures as cocatalyst.

14. The process for the hydrofluorination of a halogenated hydrocarbon which comprises reacting a halogenated hydrocarbon with hydrogen fluoride in the presence of the catalyst according to claim 11.

15. The process according to claim 14, wherein the halogenated hydrocarbon is an aliphatic alkane corresponding to the general formula $C_wH_xX_yF_z$ (I), wherein

w is an integer between 1 and 6,

x is an integer between 0 and (2w + 1),

y is an integer between 1 and (2w + 1),

z is an integer between 0 and (2w + 1),

the sum (x + y + z) has the value (2w + 2) and

X represents chlorine or bromine.

16. The process according to claim 14, wherein the halogenated hydrocarbon is an aliphatic alkene corresponding to the general formula $C_wH_xX_yF_z$ (I), wherein

w is an integer between 1 and 6,

x is an integer between 0 and (2w - 1),

y is an integer between 1 and (2w - 1),

z is an integer between 0 and (2w - 1),

the sum (x + y + z) has the value 2w and

X represents chlorine or bromine.

17. The process according to claim 14, wherein the reaction of the halogenated hydrocarbon with the hydrogen fluoride takes place in a gas phase.

18. A process for the synthesis of pentafluoroethane which comprises reacting hydrogen fluoride and a compound selected from the group consisting of perchloroethylene, fluorotetrachlorethane, difluorotrichloroethane, trifluorodichloroethane and chlorotetrafluoroethane.

19. The process according to claim 14, wherein difluoromethane is produced by reacting hydrogen fluoride and dichloromethane.

20. The process according to claim 14, wherein 1,1,1,2-tetrafluoroethane is produced by reacting hydrogen fluoride and a compound chosen from trichloroethylene or 2-chloro-1,1,1-trifluoroethane.

21. The process according to claim 14, wherein pentafluoroethane is produced by reacting hydrogen fluoride and a compound selected from the group consisting of perchloroethylene, fluorotetrachlorethane, difluorotrichloroethane, trifluorodichloroethane and chlorotetrafluoroethane.--

REMARKS

The applicants respectfully request that the preliminary amendment be entered prior to fee calculation and examination. Newly added claims 11-21 correspond to claims 1-10 as amended in the PCT application. No additional fee is required for the extra claims. If there are any additional fees due in connection with the filing of this response, including any fees required for an additional extension of time under 37 CFR 1.136, such an extension is requested and the Commissioner is authorized to charge or credit any overpayment to Deposit Account No. 03-2775.

A prompt and favorable action is solicited.

Respectfully submitted,

CONNOLLY BOVE LODGE & HUTZ LLP

By ____________
Ashley I. Pezzner
Reg. No. 35,646
Tel. (302) 888-6270

AIP/cam
::ODMA\MHODMA\CB;138946;1

Hydrofluorination catalyst and process

The present invention relates to a hydrofluorination catalyst based on chromium oxide used in particular to convert halogenated hydrocarbons under the action of hydrogen fluoride.

A great many catalysts have been described for the hydrofluorination reaction of halogenated aliphatic hydrocarbons under the action of hydrogen fluoride. Mention has generally been made of oxides or halides of chromium, aluminium, titanium, nickel, tin, antimony or other metals, used as such or deposited on a support, such as active charcoal, graphite or alumina.

The widely used chromium catalysts include mainly chromium fluorides, chromium oxyfluorides and chromium oxides, mainly chromium sesquioxide (Cr_2O_3).

Canadian Patent CA 861 572 discloses the synthesis and use of anhydrous chromium oxide as catalyst in hydrofluorination reactions of chlorinated or brominated hydrocarbons. However, no information is given with regard to the purity of the catalyst obtained according to the preparation processes disclosed in the patent.

Patent Application WO 92/19576 discloses the use of chromium oxide as hydrofluorination catalyst in the presence of hydrogen fluoride and its preparation by thermal decomposition of ammonium dichromate. The presence of traces of alkali metals and more particularly of potassium is very harmful to the activity of this catalyst.

It transpires that the activity of chromium oxide as hydrofluorination catalyst can vary in particular as a function of its preparation process, of its specific surface area, of its state of crystallinity, of the oxidation state of the chromium or of its amorphous nature without, however, a coherent explanation with regard to its activity being provided.

The Applicant Company has found that the catalytic activity of a catalyst based on chromium

oxide is highly dependent on the amount of ammonium salts present in the catalyst. More particularly, the Applicant Company has found that the catalytic activity of such a catalyst is inversely proportional to the amount of ammonium salts present as impurity in the catalyst.

One object of the present invention is consequently to provide a hydrofluorination catalyst based on chromium oxide which is poor in ammonium salts.

The ammonium salts present in the catalyst can exist in particular in the form of an ammonium halide, such as ammonium chloride or ammonium fluoride, or in the form of another inorganic or organic acid salt, such as ammonium nitrate, ammonium chromate, ammonium bichromate or ammonium acetate.

The catalysts according to the invention typically include less than 1% of ammonium salts. They preferably exhibit a content of ammonium salts of less than or equal to 0.5% by weight. The content of ammonium ions in the catalyst is preferably less than or equal to 0.2% by weight. Excellent results are obtained with a catalyst for which the content of ammonium ions is less than or equal to 0.1% by weight. Particularly advantageous results are obtained with a catalyst for which the content of ammonium ions is less than or equal to 0.05% by weight.

By convention, in the present description, the values mentioned for the content of ammonium salts in the catalyst according to the invention relate to the content of NH_4^+ ions with respect to the content of chromium in the catalyst, expressed in the form of Cr_2O_3.

The chromium oxide used in the catalyst according to the present invention can exhibit a variable specific surface area greater than or equal to 20 m^2/g and less than or equal to 500 m^2/g, determined according to the BET (Brunauer Emmet Teller) method. Generally, the pore volume of the catalyst, determined

according to the nitrogen adsorption method, is greater than or equal to 0.05 cm^3/g and less than or equal to 1 cm^3/g. The catalyst can be entirely amorphous or entirely crystalline, just as it can be partially amorphous and partially crystalline. The chromium oxide in the catalyst according to the invention is generally essentially in the III oxidation state but the catalyst can also comprise variable amounts of chromium in an oxidation state of greater than III, such as, for example, chromium(VI).

Typically, it can be synthesized according to one of the processes known to a person skilled in the art and more particularly either by reduction of chromium(VI) oxide (CrO_3) by an alcohol, such as ethanol, or by dehydration at high temperature of a chromium(III) hydroxide gel or by pyrolysis of ammonium dichromate. In the latter case, the chromium oxide obtained during the high-temperature (generally greater than 500°C) pyrolysis stage is generally cooled under a stream of air and washed several times until there are no more signs of ammonium ions in the washing solution.

In the catalyst according to the present invention, the chromium oxide can be used either as such, in the bulk form, or it can be deposited on a support, such as active charcoal, graphite, alumina, fluorinated alumina, magnesium oxide, and the like. The catalyst according to the invention is preferably composed of chromium oxide in the bulk form.

It can additionally comprise other metals or salts of other metals and their mixtures as cocatalysts. Mention may be made, among metals or metal salts which can generally be used, of, for example, cobalt, titanium, manganese, tin, antimony, nickel or zinc and their salts and their oxides. The metal derivatives can be incorporated in the chromium catalyst according to various processes, such as impregnation of the chromium oxide by a metal compound, by coprecipitation of precursors or by mixing and milling solid metal compounds.

It is generally advantageous to calcine the catalyst before use. Conventionally, this calcination is carried out under a stream of inert gas at a temperature greater than or equal to 200°C and less than or equal to 600°C. Advantageously, the calcination temperature is greater than or equal to 250°C and less than or equal to 450°C. The inert gas is generally chosen from nitrogen or rare gases, such as helium, argon or neon. For economic reasons, nitrogen is preferred. The calcination time is usually between 2 hours and 20 hours. The calcination time is advantageously greater than or equal to 4 hours and less than or equal to 16 hours. The calcination time is preferably greater than or equal to 6 hours and less than or equal to 14 hours.

The catalyst is generally pretreated with hydrogen fluoride before being employed in a hydrofluorination reaction. It is believed that this pretreatment converts the chromium oxide which is found at the surface to chromium oxyfluoride. This pretreatment is generally carried out in a reactor, usually that which is used for the hydrofluorination reactions according to the invention, by passing hydrogen fluoride over the calcined and dried chromium oxide, so as to saturate the chromium oxide with hydrogen fluoride. This pretreatment usually takes place over a period of time ranging from 15 to 300 minutes at a temperature generally of between 200 and 700°C. This pretreatment is often useful but is not essential for the satisfactory operation of the process according to the present invention.

Whatever the method of preparation of the chromium oxide, it is particularly advantageous for the pretreatment with hydrogen fluoride to be carried out on a catalyst based on chromium oxide which is poor or which has been depleted beforehand in ammonium salts.

Another subject-matter of the present invention is a method for the preparation of a catalyst based on chromium oxide which is poor in ammonium salts,

typically either by calcination of an appropriate chromium compound at a temperature of 300 to 500°C, preferably while flushing with an inert gas, such as nitrogen, or by washing the crude chromium oxide with water, optionally followed by a stage of processing the chromium oxide with other constituents of the catalyst, by calcination and by treatment with hydrogen fluoride.

Another object of the present invention is to provide a process for the hydrofluorination of halogenated hydrocarbons by the action of hydrogen fluoride on a halogenated hydrocarbon in the presence of such a catalyst.

The term "hydrofluorination" is understood to mean the addition reaction of hydrogen fluoride to a carbon-carbon double bond and the substitution reaction of a halogen atom, generally chlorine or bromine, by a fluorine atom on a saturated substrate.

In the context of the present invention, the hydrofluorination reactions take place under the catalytic action of the catalyst based on chromium oxide, introduced as such into the reaction mixture or fluorinated beforehand by reaction with hydrogen fluoride.

The halogenated hydrocarbon used in the process according to the invention can be an aliphatic alkane corresponding to the general formula $C_wH_xX_yF_z$ (I), in which w is an integer between 1 and 6, x is an integer between 0 and (2w +1), y is an integer between 1 and (2w +1), z is an integer between 0 and (2w +1), the sum (x + y + z) has the value (2w +2) and X represents chlorine or bromine. Advantageously, the halogenated hydrocarbon used in the process according to the invention is an aliphatic alkane corresponding to the formula (I) in which w is an integer between 1 and 4 and x is an integer between 1 and 2w.

Mention may be made, as non-limiting examples of halogenated alkanes used in the process according to the invention, of dichloromethane, chlorofluoromethane, chlorodifluoromethane, 1-chloro-1-fluoroethane, 1,1-di-

chloro-1-fluoroethane, 1-chloro-1,1-difluoroethane, chlorotetrafluoroethane isomers, dichlorotrifluoroethane isomers, trichlorodifluoroethane isomers, tetrachlorofluoroethane isomers, pentachloroethane or compounds of general formulae $C_3H_3Cl_{(5-z)}F_z$ and $C_4H_5Cl_{(8-z)}F_z$ with z representing an integer which can take the values from 1 to 4.

The halogenated hydrocarbon used in the process according to the invention can also be an aliphatic alkene corresponding to the general formula $C_wH_xX_yF_z$ (I), in which w is an integer between 1 and 6, x is an integer between 0 and (2w - 1), y is an integer between 1 and (2w - 1), z is an integer between 0 and (2w - 1), the sum (x + y + z) has the value 2w and X represents chlorine or bromine. The halogenated hydrocarbon used in the process according to the invention can also advantageously be an aliphatic alkene corresponding to the formula (I) in which w is an integer between 1 and 4.

Mention may be made, as non-limiting examples of halogenated alkenes used in the process according to the invention, of 1,1-dichloroethylene, trichloroethylene, perchloroethylene, vinyl chloride, 3,3,3-trichloroprop-1-ene, 1,1,3-trichloroprop-1-ene, 1,1,3,3-tetrachlorobut-1-ene, 1,1,1,3-tetrachlorobut-2-ene, 1,1,1,3-tetrachlorobut-3-ene, 1,1,4,4,4-pentachlorobut-1-ene, 1,1,1,3-tetrachloroprop-2-ene, 1,1,3,3-tetrachloroprop-1-ene, 1,1,3,3-tetrachloro-2-methylprop-2-ene, 1,1,1,3-tetrachloro-2-methylprop-2-ene, 1,1,1,3,3-pentachloroprop-2-ene, 3-chloro-1,1,1-trifluoroprop-2-ene and the mixtures of these compounds.

An aim of the invention is thus to produce, starting from saturated or unsaturated halogenated hydrocarbons, fluorinated or chlorofluorinated alkanes which comprise more fluorine atoms and fewer chlorine atoms than the reactants used. The invention is targeted in particular at the synthesis of fluorinated hydrocarbons, such as in particular difluoromethane, pentafluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-

trifluoroethane, 1,1-difluoroethane, 2,2-dichloro-1,1,1-trifluoroethane, 1,1,1-trifluoro-2-chloroethane, 1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane, 1,1,1,3,3,3-hexafluorobutane, 1,1,1,3,3-pentafluoro-2-methylpropane and 1,1,1,3,3,3-hexafluoropropane. A more particular aim of the invention is the preparation of fluorinated alkanes not comprising a chlorine atom under the catalytic action of a chromium oxide which is poor in ammonium salts.

A more particular aim of the invention is to produce, under the action of the catalyst according to the invention, pentafluoroethane by hydrofluorination of perchloroethylene, difluoromethane by hydrofluorination of dichloromethane, 1,1,1,2-tetrafluoroethane by hydrofluorination of 2-chloro-1,1,1-trifluoroethane and 2-chloro-1,1,1-trifluoroethane by hydrofluorination of trichloroethylene.

The hydrofluorination reaction can be carried out in the gas phase or in the condensed phase. The gas phase is preferred.

The process according to the present invention is generally carried out continuously.

The molar ratio of the hydrogen fluoride to the halogenated hydrocarbon employed is usually greater than or equal to 1 and less than or equal to 100. This molar ratio is advantageously greater than or equal to 3 and less than or equal to 50. This molar ratio is preferably greater than or equal to 4 and less than or equal to 20.

The reaction pressure is not critical. A pressure of between 1 and 10 bar is usually highly suitable.

The reaction temperature is generally between ambient temperature and 600°C. The reaction temperature is advantageously greater than or equal to 100°C and less than or equal to 500°C. The reaction temperature is preferably greater than or equal to 200°C and less than or equal to 450°C.

Generally, the higher the reaction temperature, the greater the HF/halogenated hydrocarbon molar ratio and the longer the contact time, the higher the degree of conversion of the reactants to fluorinated hydrocarbons and the greater the degree of hydrofluorination. The parameters mentioned above can be adjusted so as to obtain the desired product with high selectivity, a high degree of conversion and a high yield.

The unconverted reactants and the intermediate compounds can advantageously be recycled in the hydrofluorination reactor to increase the productivity with respect to the desired fluorinated product.

The process according to the invention can be carried out in any type of reactor or apparatus which is resistant to pressure, to hydrogen fluoride and to hydrogen chloride and, in the case of a continuous process, which makes it possible to continually maintain a substantially stable composition of the reaction mixture. The process according to the invention is generally carried out continuously in a gas phase reactor equipped with a device for introducing the reactants, in the liquid or gas phase, and for withdrawing a gas stream, for example in a tubular reactor filled with a stationary catalyst bed.

The optimum residence time, expressed as the ratio of the total throughput of the reactants (at reaction temperature and pressure) to the free volume of the reactor, can generally vary from 5 seconds to 10 minutes.

The examples below illustrate the invention without implied limitation. In these examples, the degree of conversion of the halogenated hydrocarbon is the ratio of the amount employed, decreased by the amount unconverted, to the amount employed, multiplied by 100; the selectivity for fluorinated or chlorofluorinated alkane is the ratio of the amount of fluorinated or chlorofluorinated alkane formed to the amount which would have been formed if all the

halogenated hydrocarbon converted had generated fluorinated or chlorofluorinated alkane; the overall selectivity is the sum of the selectivities of all the intermediates which can be recovered as the desired fluorinated or chlorofluorinated alkane; the yield of fluorinated or chlorofluorinated alkane is the product of the degree of conversion by the selectivity for this fluorinated or chlorofluorinated alkane.

Examples 1-10

20 cm^3 of bulk chromium oxide including a variable content of NH_4^+ and a hydrogen fluoride/perchloroethylene (PER) mixture in a molar ratio of 10 mol/mol were introduced into a cylindrical autoclave with an internal diameter of 15 mm. The reaction pressure was maintained at 1 bar and the temperature at 350°C. The residence time was 12.5 seconds. The main product obtained is 1,1,1,2,2-pentafluoroethane (HFC-125).

The results are collated in Table I below.

Table I

Test No.	$[NH_4^+]$ (%)	Degree of conversion of the PER (%)	Yield of HFC-125 (mol%)	Overall selectivity (mol%)
1	0.27	43	12	73
2	0.17	63	30	79
3	0.11	69	34	81
4	0.07	85	47	80
5	0.05	96	58	81
6	0.001	95	58	85
7	0.001	96	59	85
8	0.001	97	60	84
9 (C)	6.5	7	0.2	85

(C) indicates a comparative example, not in accordance with the invention.

CLAIMS

1. Hydrofluorination catalyst based on chromium oxide which is poor in ammonium salts.

2. Catalyst according to Claim 1, comprising less than 1% by weight of ammonium salts, expressed in the form of NH_4^+, with respect to the content of chromium in the catalyst, expressed in the form of Cr_2O_3.

3. Catalyst according to Claim 2, in which the content of ammonium salts is less than or equal to 0.2% by weight of ammonium salts.

4. Process for the hydrofluorination of a halogenated hydrocarbon by reaction with hydrogen fluoride in the presence of a catalyst according to either one of Claims 2 and 3.

5. Process according to Claim 4, in which the halogenated hydrocarbon is an aliphatic alkane corresponding to the general formula $C_wH_xX_yF_z$ (I), in which w is an integer between 1 and 6, x is an integer between 0 and (2w + 1), y is an integer between 1 and (2w + 1), z is an integer between 0 and (2w + 1), the sum (x + y + z) has the value (2w + 2) and X represents chlorine or bromine.

6. Process according to Claim 4, in which the halogenated hydrocarbon is an aliphatic alkene corresponding to the general formula $C_wH_xX_yF_z$ (I), in which w is an integer between 1 and 6, x is an integer between 0 and (2w - 1), y is an integer between 1 and (2w - 1), z is an integer between 0 and (2w - 1), the sum (x + y + z) has the value 2w and X represents chlorine or bromine.

7. Process according to any one of Claims 4 to 6, in which the reaction of the halogenated hydrocarbon with the hydrogen fluoride takes place in the gas phase.

8. Process according to any one of Claims 4 to 7 for the synthesis of pentafluoroethane by reaction between hydrogen fluoride and a compound chosen from perchloroethylene, fluorotetrachlorethane, difluoro-

trichloroethane, trifluorodichloroethane and chlorotetrafluoroethane.

9. Process according to any one of Claims 4 to 7 for the synthesis of difluoromethane by reaction between hydrogen fluoride and dichloromethane.

10. Process according to any one of Claims 4 to 7 for the synthesis of 1,1,1,2-tetrafluoroethane by reaction between hydrogen fluoride and a compound chosen from trichloroethylene and 2-chloro-1,1,1-trifluoroethane.

ABSTRACT

Hydrofluorination catalyst and process

Hydrofluorination catalyst based on a chromium oxide which is poor in ammonium salts.

098124

COMBINED DECLARATION AND POWER OF ATTORNEY

Atty. Docket No.:

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

"Hydrofluorination catalyst and process"

the specification of which

(check one) ☐ is attached hereto.

☐ was filed on as Application and amended through .

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) — Priority Claimed

(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
09800732	Belgium	12 October 1998	■	☐
			☐	☐

I hereby claim benefits under Title 35, United States Code, §119 of any United States provisional application(s) listed below:

(Application Serial No.)	(Filing Date)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
PCT/EP99/07782	11 October 1999	Filing

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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